

AN INVESTIGATION OF THE VELOCITY OF CRYSTALLIZATION  
OF UNDERCOOLED BENZENE

by

WILLIAM ALBERT BARTER

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## INTRODUCTION

Most fluids when cooled within a certain range below their normal melting point will remain fluid for an indefinite period of time if not disturbed. If a sample of a fluid in such a metastable condition is disturbed by the introduction of a seed crystal it will solidify. If the sample is small, such as that held by a watch glass, the solidification or crystallization of some fluids is seemingly instantaneous. This phenomenon is noted for benzene ( $C_6H_6$ ) as well as for many other substances.

When such a sample is undercooled in a large enough quantity and distributed as in a long tube, the velocity with which crystallization proceeds after "triggering" is observed to be finite. Furthermore the velocity is observed to vary directly with the degree of undercooling.

In this experiment an attempt is made to show how the velocity of crystallization of benzene varies with degree of undercooling. The results will be compared to a similar experiment performed with liquid phosphorous Powell, et al. (4) and with theory. An empirical equation is then proposed which will fit the data.

## EQUIPMENT AND PROCEDURE

The sample holder was constructed of two concentric pyrex glass tubes of 10mm and 6mm outside diameters. The wall of the outside tube was approximately 1mm thick. The system was sealed in such a way that the only entry was through the side arm at the top. Distilled and sodium dried benzene was pipetted through this side arm to a level about one inch above the bottom end of the inside tube. This arrangement formed at the top of the sample, a one inch well which could be used to initiate freezing without contamination.

The cooling bath consisted of a transparent glass container filled with commercial ethanol. The container had to be constructed in the manner of a Dewar flask in order to promote efficient cooling and to prevent frosting. The outside diameters of the walls of the container were 51mm and 32mm. Construction of the sample holder and the cooling bath is shown in Plate I.

The bath was cooled by passing a continuous flow of dry air through a copper coil immersed in a dry ice-acetone solution and then through a copper U-tube immersed in the ethanol. The temperature of the bath was controlled by varying the flow of air.

Temperature observations were made with a double junction, copper-constantan thermocouple and a Rubicon potentiometer. One junction of the thermocouple was enclosed in a glass sleeve and immersed, along with the sample holder, in the ethanol bath. The reference junction was kept in a water-ice bath. A stirring mechanism was devised to eliminate the temperature gradient. The pressure on the sample was maintained at 760mm by connecting a manometer to the side arm of the sample holder.

When the system had reached an equilibrium temperature, freezing was initiated. This was done by introducing a small piece of dry ice into a few drops of acetone kept in the bottom of the well of the sample holder.

Data were recorded on Dupont 16mm, 931A, Rapid Reversal, fine grain, high speed, motion picture film. The camera, a Bell and Howell, Filmo 70, was placed about 20 inches from the location of the sample holder in the bath. A millimeter scale was taped along the side of the bath, parallel to the sample and at the same distance from the camera. The camera was calibrated with a stroboscope to run at 40 frames per second. A ten second sweep clock was included in the picture of the system as a check on the timing for all runs. The clock revealed that the camera speed was accurate to  $\pm 1$  frame per second throughout the experiment.

EXPLANATION OF PLATE I

Fig 1. Cooling Bath

A. Vacuum

B. Ethanol

Fig 2. Sample Holder

A. Benzene

B. Acetone

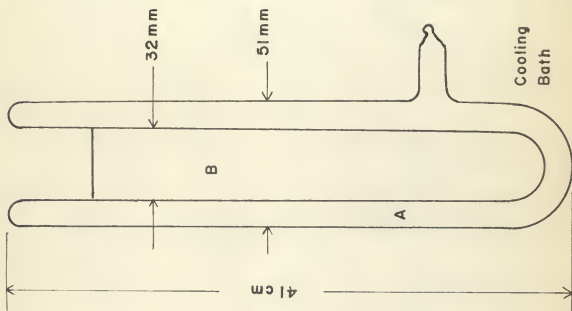


Fig. 1

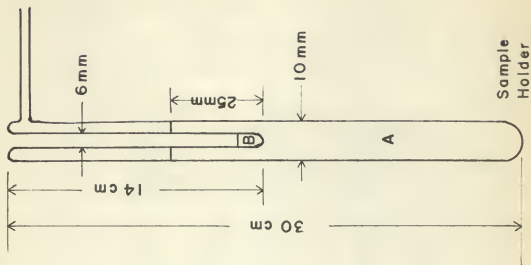


Fig. 2

The data were taken by observing the film with a movie film and microfilm viewer in which the individual frame was enlarged to approximately 19 times its actual size. The position of the front of the advancing crystal growth was recorded approximately 4cm on either side of the location of the thermocouple junction in order to eliminate the effect of any temperature gradient. The time of this transit of the front was determined by counting the number of frames involved. Velocity was determined by the slope of a plot of position versus time. In some cases a slight curvature was noticed, which was probably caused by a small temperature gradient. In any case the velocity was determined by fitting the best straight line to the points. The data appear in Table I.

#### RESULTS

The velocity of crystallization of benzene was plotted as a function of temperature as shown in Plate II. Powell, et al. (4) obtained a similar plot for liquid phosphorous, as shown in Plate III. The velocity does not appear to approach a maximum in either case, for the temperature ranges used. The results for liquid phosphorous were closely reproduced by the authors with the equation  $(V\gamma)^{1/2} = \text{const } (T_0 - T)$  where  $\gamma$  is the viscosity and  $T_0$  the melting point. A plot of  $(V\gamma)^{1/2}$  versus  $T$  for benzene shows a definite curvature as seen in Plate IV. This is contrary to the results for liquid phosphorous.

The amount of undercooling achieved by Powell, Gilman and Hildebrand for liquid phosphorous was approximately 22° C below the melting point of 44.1° C. Below that temperature the sample froze spontaneously. The velocity of crystallization at this lowest temperature was of the order of 210 cm/sec. Even at this high velocity the authors decided that the sleeve of the solid next to

Table 1. Temperatures in millivolts and corresponding temperatures in degrees centigrade\*; also the corresponding velocities.

Temperature (mv)	:	Temperature (°C)	:	Velocity (cm/sec)
+0.102	:	+2.6	:	1.6
+0.062	:	+1.5	:	1.6
+0.025	:	+0.6	:	4.0
-0.040	:	-1.1	:	5.7
-0.096	:	-2.5	:	11.7
-0.150	:	-3.9	:	15.6
-0.204	:	-5.3	:	20.5
-0.166	:	-4.3	:	17.8
-0.251	:	-6.6	:	29.6
-0.226	:	-5.9	:	28.0
-0.188	:	-5.0	:	20.6
-0.131	:	-3.4	:	14.0
-0.114	:	-3.0	:	14.9
-0.070	:	-1.8	:	8.4
-0.008	:	-0.2	:	5.9
+0.041	:	+1.0	:	2.6
+0.086	:	+2.2	:	1.0
-0.216	:	-5.6	:	23.4
-0.245	:	-6.4	:	27.4
-0.172	:	-4.5	:	15.6
-0.087	:	-2.3	:	9.4
-0.052	:	-1.4	:	5.9
-0.026	:	-0.7	:	4.9
-0.003	:	-0.1	:	5.3
+0.015	:	+0.3	:	3.1
+0.055	:	+1.4	:	2.3
+0.075	:	+1.9	:	1.5

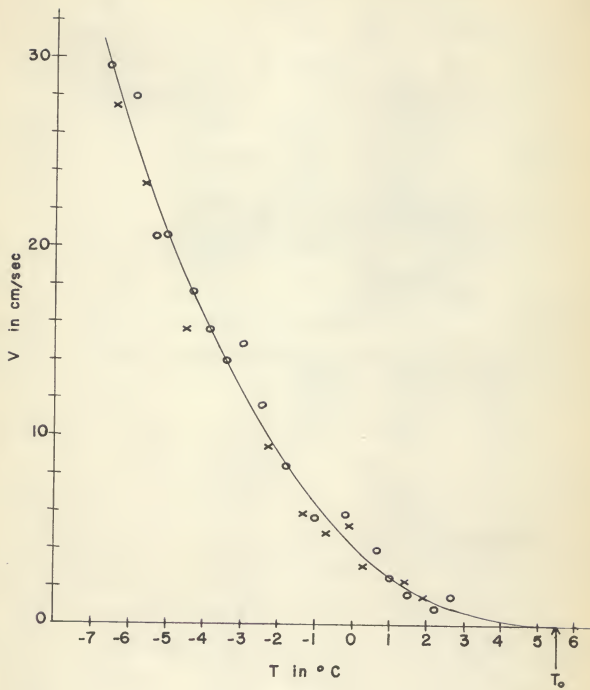
\* Temperature in degrees corresponding to that in millivolts for a copper-constantan thermocouple was determined from data by Dika (2).

EXPLANATION OF PLATE II

Plot of velocity of crystallization of benzene  
versus temperature.

- o Data taken during one 12 hour period.
- x Data taken 3 days later using the same  
sample.

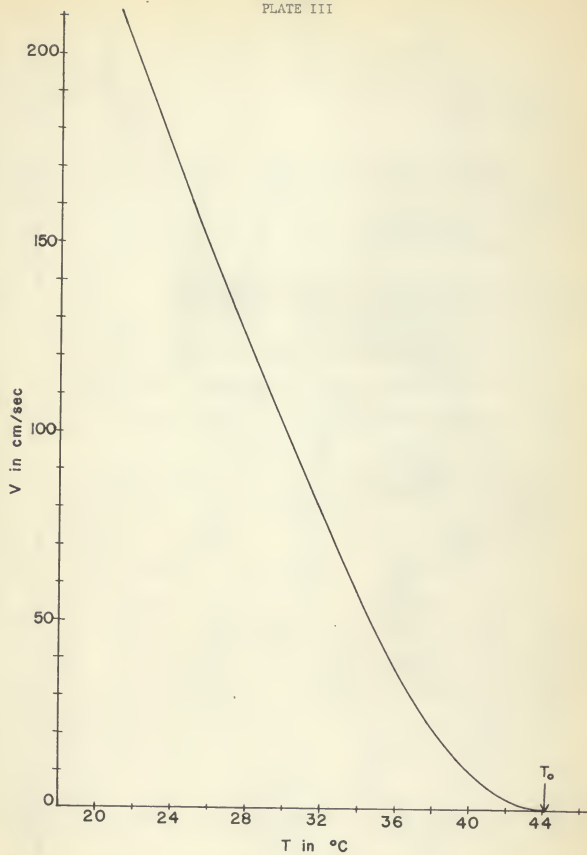
PLATE II



EXPLANATION OF PLATE III

Plot of velocity of crystallization of liquid phosphorus versus temperature from work by Powell, Gilman and Hildebrand (4).

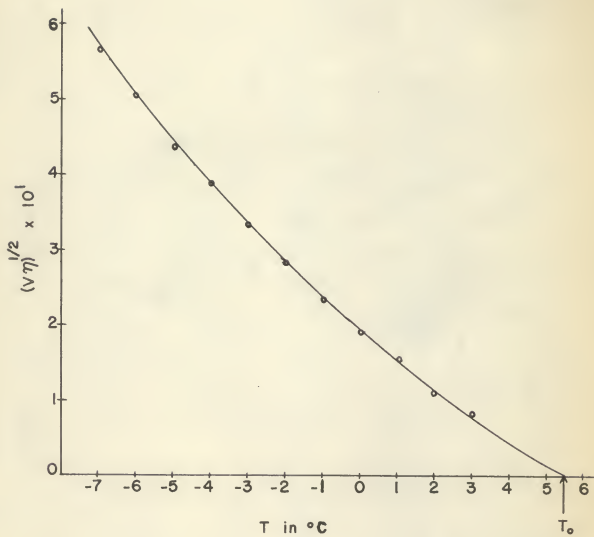
PLATE III



#### EXPLANATION OF PLATE IV

A plot of  $(V\gamma)^{1/2}$  versus temperature where the values of  $V$  were taken from a best fit of the experimental data for benzene. Values of  $\gamma$  were determined from an extrapolation of values from the Handbook of Physics and Chemistry (6).

## PLATE IV



the bath was formed at nearly the bath temperature. Their decision was based on the assumption that the heat of fusion for the solid forming nearest the bath was conducted away through the wall of the glass tube to the bath rapidly enough to result in a nearly isothermal process. The front of crystallization near the center of the tube must advance more slowly. This phenomenon is actually observed with benzene. The above assumption seems even more probable in the present case since the maximum velocity attained was only on the order of 30 cm/sec. One cannot attribute this "sleeve" phenomenon to a temperature gradient, for the sleeve was observed for approach to the desired temperature either from above or below that temperature. Bono (1) mentioned in his work with xylenes that the velocity of crystallization was slightly decreased when the thickness of the glass tube was increased from 1.25mm to 3.00mm, while holding all other parameters constant. Considering a specific example, the velocity was decreased by about 7% from 3.6 cm/sec. It is difficult to imagine any other reason for this than that the conduction of the heat of fusion from the system is more easily accomplished for the thinner walls.

#### DISCUSSION

Turnbull (5) has presented a theory of phase boundary migration for a one component system where the effects due to density change are ignored. Consider the special case for a liquid (a) to solid (b) transition at an undercooling of  $T_0 - T$ . A molecule in order to cross the interface from the liquid to the solid must acquire an activation energy  $\Delta G$ . The frequency of transfer of a molecule in this direction is

$$(1) \quad \nu_{ab} = \nu_0 \exp (-\Delta G/kT)$$

where  $\nu_0$  is the frequency of the molecule striking the "barrier". If  $\Delta G'$  is

the difference in Gibbs potentials per molecule between liquid and solid, the frequency of transfer in the opposite direction is

$$(2) \quad \nu'_{ba} = \nu_o \exp [-(\Delta G + \Delta G')/kT]$$

The net frequency of transfer of molecules across the phase boundary is

$$(3) \quad \nu = \nu_{ab} - \nu'_{ba}$$

and the velocity of migration of this boundary is proportional to  $\nu$ . Then

$$(4) \quad V = C \exp (-\Delta G/kT) [1 - \exp (-\Delta G'/kT)]$$

where C is the constant of proportionality.

From the basic laws of thermodynamics, if we neglect density changes and consider a one component system at constant pressure, Gibbs potential can be expressed as

$$(5) \quad dG_a = -S_a dT \qquad dG_b = -S_b dT$$

where  $S_a$  and  $S_b$  are the entropies referred to one molecule at temperature T.

Integrating from normal equilibrium point  $G(p_o, T_o)$  to  $G(p_o, T)$

$$(6) \quad G_a - G_a^o = - \int_{T_o}^T S_a dT \qquad G_b - G_b^o = - \int_{T_o}^T S_b dT$$

Subtracting we get

$$(7) \quad (G_a - G_b) - (G_a^o - G_b^o) = - \int_{T_o}^T (S_a - S_b) dT$$

But

$$(8) \quad S_a - S_b = - \lambda/T$$

where  $\lambda$  is the latent heat of fusion per molecule. We know also that at the normal equilibrium point  $G_a^o = G_b^o$  so

$$(9) \quad G_a - G_b = \Delta G' = \lambda \int_{T_o}^T dT/T$$

and finally

$$(10) \quad \Delta G' = \lambda \ln T/T_o.$$

The resulting expression for velocity of crystallization in an undercooled liquid is then

$$(11) \quad V = C \exp \left( \frac{-\Delta G}{kT} \right) \left[ 1 - \exp \frac{-\lambda \ln(T/T_o)}{kT} \right]$$

The constants  $C$  and  $\Delta G$  were evaluated from the two equations which result when the experimental values of  $V$  at temperatures  $-4$  and  $-6^{\circ}\text{C}$  were substituted in equation (11). It was found that the expression fits the experimental data reasonably well for  $C = \exp(-36.72)$  and  $\Delta G = -1.54 \times 10^{-12}$ . The expression is plotted on Plate V.

A negative activation energy, however, does not have any physical meaning when one considers its definition. Moreover, the value for  $C$  is unreasonable. It is therefore difficult to give the theoretical expression any physical interpretation. At best equation (11) can be considered an empirical equation which approximately fits the data.

The fault with the above expression may lie in the derivation of  $\Delta G'$ . The thermodynamics of reversible processes was employed, which implies that a near equilibrium condition exists. This is definitely not the case for the solidification of an undercooled liquid, which may account for the unacceptable values of  $C$  and  $\Delta G$  obtained in Turnbull's equation.

Frenkel (3) has implied that the rate of a change in phase from liquid to solid must be inversely proportional to the viscosity. This was born out by the results obtained by Powell, Gilman and Hildebrand for liquid phosphorous. If it is assumed that the velocity of crystallization of benzene depends on viscosity in this same way, a modification of Turnbull's theory can be made. This can be done by replacing the quantity  $\lambda \ln T/T_0$ , which was derived on the basis of reversible thermodynamics, by an arbitrary function of the temperature which is to be determined from the measured velocities.

If  $\Delta G$  is assigned the value of the activation energy associated with diffusion, Turnbull's expression can be written as

$$(12) \quad V = \frac{C}{\eta} f(T)$$

# EXPLANATION OF PLATE V

Plot of V versus T from the expression

$$V = C \exp(-\Delta G/kT) \left[ 1 - \exp \frac{-\lambda \ln T/T_0}{kT} \right]$$

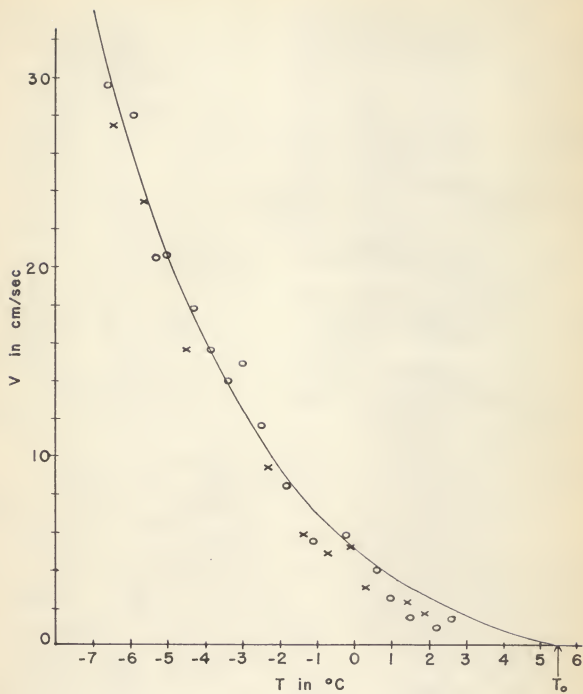
superimposed on the experimental points for benzene where

$$C = \exp(-36.72)$$

and

$$\Delta G = -1.54 \times 10^{-12}.$$

PLATE V



where  $f(T) = 1 - \exp\left(\frac{-\Delta G'}{kT}\right)$ . If  $\Delta G'$  can be written as

$$(13) \quad \Delta G' = g(T_0 - T) = \sum_{n=1}^{\infty} C_n (T_0 - T)^n$$

(where the sum must begin with  $n = 1$  in order that  $\Delta G'$  vanish at  $T = T_0$ ),

then a Taylor's expansion of  $f(T)$  about  $T_0$  can be written

$$(14) \quad f(T) = \frac{-C_1}{k} \left[1 - \frac{T}{T_0}\right] + \left[\frac{C_2 T_0}{k} - \frac{C_1}{k} - \frac{1}{2} \left(\frac{C_1}{k}\right)^2\right] \left[1 - \frac{T}{T_0}\right]^2 \\ + \left[-\frac{C_3 T_0^2}{k} + \frac{C_2 T_0}{k} - \frac{C_1}{k} - \left(\frac{C_1}{k}\right)^2 + \frac{C_1 C_2 T_0}{k^2} - \frac{1}{6} \left(\frac{C_1}{k}\right)^3\right] \left[1 - \frac{T}{T_0}\right]^3 + \dots$$

$\Delta G'$  is considered as the positive increase of the barrier  $\Delta G$  seen by a molecule in the solid, and moreover, it must remain positive as long as  $T_0$  is greater than  $T$ . As  $T$  approaches very near  $T_0$ , the first term in the series of equation (13) becomes the dominant one. Therefore  $C_1$  must be a positive number.

However, if  $C_1$  is positive then from equation (14)  $f(T)$  and therefore  $V$  must become negative as  $T$  approaches  $T_0$ . This is not a possible situation so  $C_1$  must be zero or at least negligibly small. Equation (14) then becomes

$$(15) \quad f(T) = \frac{C_2}{kT_0} (T_0 - T)^2 + \left[\frac{C_2}{kT_0^2} - \frac{C_3}{kT_0}\right] (T_0 - T)^3 + \dots$$

If all but the second order term can be neglected the velocity expression is equivalent to that found for liquid phosphorous above. However, it has been shown that this does not hold for benzene. If the third order term is included the velocity becomes of the form

$$(16) \quad V = \frac{C'}{\gamma} (B \Delta T^2 + \Delta T^3)$$

Evaluating the constants  $C'$  and  $B$  from experimental points of the benzene data  $V$  becomes

$$(17) \quad V = \frac{0.0123}{\gamma} (3.99 \Delta T^2 + \Delta T^3)$$

This expression fits the experimental points quite well as shown in Plate VI.

Equation (17) reaches a maximum at a temperature of approximately  $-90^\circ \text{C}$ .

This value is reasonable since there is no indication that the measured velocity is approaching a maximum at  $-60^\circ \text{C}$ .

EXPLANATION OF PLATE VI

Plot of  $V$  versus  $T$  from the expression

$$V = \frac{C'}{7} (B\Delta T^2 + \Delta T^3)$$

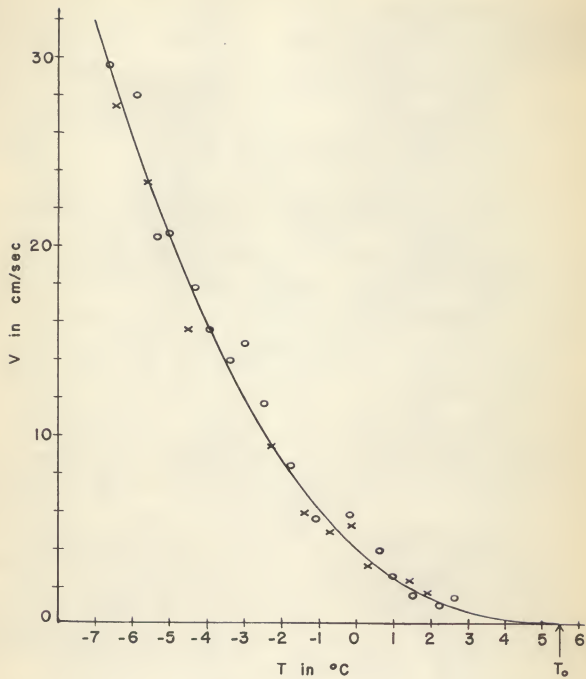
superimposed on the experimental points for benzene where

$$C' = 0.0123$$

and

$$B = 3.99.$$

PLATE VI



## CONCLUSION

It would seem that the form of Turnbull's expression is correct but that the derivation of  $\Delta G'$  by means of ordinary thermodynamic expressions is not. The assumption that the velocity of crystallization is inversely proportional to the viscosity of the liquid appears to be acceptable. Equation (17), though physically reasonable, must be considered empirical until the two constants  $C'$  and  $B$  are given physical meaning.

Special note should be taken of the agreement between the expression found by Gilman, Powell and Hildebrand and that derived in this paper from the theory of Turnbull. The only difference was the appearance of the term  $\Delta T^3$ . A correction of some sort might be expected for substances which do not have the spherical symmetry of monatomic molecules. It would be of interest to investigate the velocity of crystallization of an undercooled liquid of even more complicated molecular structure.

## ACKNOWLEDGMENTS

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It was observed that undercooled benzene freezes at a finite rate. It was also observed that the rate of freezing depends in a direct way on the degree of undercooling.

A sample of benzene was cooled to various temperatures below its melting point and crystallization was initiated. The progress of the crystal growth was recorded with a motion picture camera running at a calibrated speed of 40 frames per second. The velocity of the progress, as taken from the film, was plotted as a function of the temperature. The results were compared with similar work done on liquid phosphorous.

A treatment of a theoretical expression based on the theory of reaction rates resulted in an approximate fit to the experimental data, but gave rise to constants which could not be given a satisfactory interpretation. A somewhat different treatment of the theory resulted in the more satisfactory equation:

$$v = \frac{0.0121}{7} (3.99 \Delta T^2 + \Delta T^3).$$